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C250 C251 C252 C253 C254 C255 C256 C28X  
C280 C281 C282 C30Y C31Y C311 C313 C314  
C315 C32Y C321 C322 C323 C324 C326 C329  
C332 C338 C339 C34Y C341 C342 C345 C346  
C35X C350 C351 C352 C355 C36Y C360 C361  
C362 C364 C365 C366 C368 C380 C381 C385  
C39Y C395 C51X C510 C531 C535 C57Y C574  
C58X C58Y C580 C584 C589 C596 C60X C60Y  
C62X C620 C623 C626 C628 C63X C634 C644  
C65X C652 C658 C66X C660 C662 C664 C668  
C669 C672 C682 C694 C695 C697 C699 C71X  
C80Y C800 C802 C805  
C2R RSGNC RS142 RS152 RS163 RS169 RS205  
RS208 RS212 RS222 RS352 RS369

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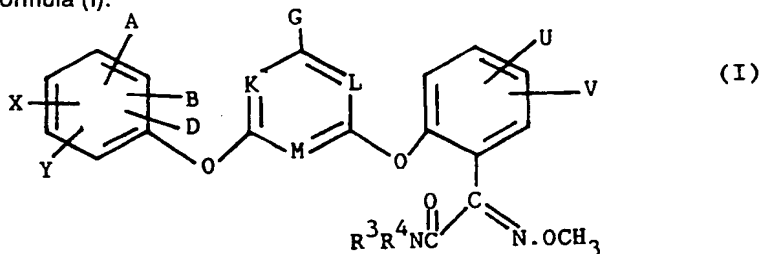
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(54) Pyrimidine fungicides

(57) Compounds having the formula (I):



in which any two of K, L and M are nitrogen and the other is CE; X and Y are independently hydrogen, halogen, C<sub>1-4</sub> alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>2-8</sub> alkenyl, C<sub>2-8</sub> alkynyl, C<sub>2-4</sub> alkynyloxy, phenyl, benzyloxy, cyano, isocyano, isothiocyanato, nitro, NR<sup>1</sup>R<sup>2</sup>, NR<sup>1</sup>OR<sup>2</sup>, N<sub>3</sub>, NHCOR<sup>1</sup>, NR<sup>1</sup>CO<sub>2</sub>R<sup>2</sup>, NHCONR<sup>1</sup>R<sup>2</sup>, N=CHNR<sup>1</sup>R<sup>2</sup>, NHSO<sub>2</sub>R<sup>1</sup>, OR<sup>1</sup>, OCOR<sup>1</sup>, OSO<sub>2</sub>R<sup>1</sup>, SR<sup>1</sup>, SOR<sup>1</sup>, SO<sub>2</sub>R<sup>1</sup>, SO<sub>2</sub>OR<sup>1</sup>, SO<sub>2</sub>NR<sup>1</sup>R<sup>2</sup>, COR<sup>1</sup>, CR<sup>1</sup>=NOR<sup>2</sup>, CHR<sup>1</sup>CO<sub>2</sub>R<sup>2</sup>, CO<sub>2</sub>R<sup>1</sup>, CONR<sup>1</sup>R<sup>2</sup>, CSNR<sup>1</sup>R<sup>2</sup>, CH<sub>3</sub>O<sub>2</sub>C.C:CH.OCH<sub>3</sub>, 1-(imidazol-1-yl), vinyl, a 5-membered heterocyclic ring containing one, two or three nitrogen heteroatoms, or a 5- or 6-membered heterocyclic ring containing one or two oxygen or sulphur heteroatoms, optionally a nitrogen heteroatom and optionally one or two oxo or thioxo substituents; or X and Y, when *ortho* to one another, join to form a 5- or 6-membered aliphatic or aromatic ring optionally containing one or two oxygen, sulphur or nitrogen atoms or one, two or three nitrogen atoms; A, B, D, E, G, U and V are independently hydrogen, halogen, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxy, cyano, nitro or trifluoromethyl; and R<sup>1</sup> and R<sup>2</sup> are independently hydrogen, C<sub>1-4</sub> alkyl, C<sub>2-8</sub> alkenyl or phenyl, can be applied to plants or seeds for the control of fungi.

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FUNGICIDES

This invention relates to derivatives of O-methyl oxyiminoacetamide useful as fungicides, to processes for preparing them, to fungicidal compositions containing them, and to methods of using them to combat fungi, especially fungal infections of plants.

According to the present invention there are provided pyrimidines having the formula (I), in which any two of K, L and M are nitrogen and the other is CE; X and Y are independently hydrogen, halogen, C<sub>1-4</sub> alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>2-8</sub> alkenyl (including C<sub>2-4</sub> alkenyl), C<sub>2-8</sub> alkynyl (including C<sub>2-4</sub> alkynyl), C<sub>2-4</sub> alkynyloxy, phenyl, benzyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, NR<sup>1</sup>R<sup>2</sup>, NR<sup>1</sup>OR<sup>2</sup>, N<sub>3</sub>, NHCOR<sup>1</sup>, NR<sup>1</sup>CO<sub>2</sub>R<sup>2</sup>, NHCONR<sup>1</sup>R<sup>2</sup>, N=CHNR<sup>1</sup>R<sup>2</sup>, NHSO<sub>2</sub>R<sup>1</sup>, OR<sup>1</sup>, OCOR<sup>1</sup>, OSO<sub>2</sub>R<sup>1</sup>, SR<sup>1</sup>, SOR<sup>1</sup>, SO<sub>2</sub>R<sup>1</sup>, SO<sub>2</sub>OR<sup>1</sup>, SO<sub>2</sub>NR<sup>1</sup>R<sup>2</sup>, COR<sup>1</sup>, CR<sup>1</sup>=NOR<sup>2</sup>, CHR<sup>1</sup>CO<sub>2</sub>R<sup>2</sup>, CO<sub>2</sub>R<sup>1</sup>, CONR<sup>1</sup>R<sup>2</sup>, CSNR<sup>1</sup>R<sup>2</sup>, CH<sub>3</sub>O<sub>2</sub>C.C:CH.OCH<sub>3</sub>, 1-(imidazol-1-yl)vinyl, a 5-membered heterocyclic ring containing one, two or three nitrogen heteroatoms, or a 5- or 6-membered heterocyclic ring containing one or two oxygen or sulphur heteroatoms, optionally a nitrogen heteroatom and optionally one or two oxo or thioxo substituents; or X and Y, when ortho to one another, join to form a 5- or 6-membered aliphatic or aromatic ring optionally containing one or two oxygen, sulphur or nitrogen atoms or one, two or three nitrogen atoms; A, B, D, E, G, U and V are independently hydrogen, halogen (especially fluorine and chlorine), C<sub>1-4</sub> alkyl (especially methyl), C<sub>1-4</sub> alkoxy (especially methoxy), cyano, nitro or trifluoromethyl; R<sup>1</sup> and R<sup>2</sup> are independently hydrogen, C<sub>1-4</sub> alkyl, C<sub>2-8</sub> alkenyl (including C<sub>2-4</sub> alkenyl) or phenyl; the aliphatic moieties of any of the foregoing being optionally substituted with one or more of halogen, cyano, OR<sup>1</sup>, SR<sup>1</sup>, NR<sup>1</sup>R<sup>2</sup>, SiR<sup>1</sup><sub>3</sub> or OCOR<sup>1</sup> and the phenyl moieties of any of the foregoing being optionally substituted with one or more of halogen, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxy, nitro or cyano; and R<sup>3</sup> and R<sup>4</sup> are independently hydrogen or C<sub>1-4</sub> alkyl.

Because of the unsymmetrically substituted double bond of the oxime group, the compounds of the invention may be obtained in the form of mixtures of (E) and (Z) geometric isomers. However, these mixtures can be separated into individual isomers, and this invention embraces such isomers and mixtures thereof in all proportions including those which consist substantially of the (Z)-isomer and those which consist substantially of the (E)-isomer.

The (E)-isomer, in which the groups  $\text{-CONR}^3\text{R}^4$  and  $\text{-OCH}_3$  are on opposite sides of the double bond of the oxime group, are the more fungicidally active and form a preferred embodiment of the invention.

Alkyl groups contain from 1 to 4 carbon atoms and may be in the form of straight or branched chains. Examples are methyl, ethyl, iso-propyl, n-butyl and t-butyl. Cycloalkyl groups contain from 3 to 6 carbon atoms and include cyclopropyl and cyclohexyl.

Alkenyl and alkynyl groups contain from 2 to 8 carbon atoms, typically from 2 to 4 carbon atoms, and may be in the form of straight or branched chains. Examples are ethenyl, allyl, methylallyl and propargyl.

Halogen is typically fluorine, chlorine or bromine.

Substituted aliphatic moieties include, in particular,  $\text{halo}(\text{C}_{1-4})\text{alkyl}$ ,  $\text{halo}(\text{C}_{1-4})\text{alkoxy}$ ,  $\text{halo}(\text{C}_{1-4})\text{alkylthio}$ ,  $\text{CH}_2\text{OR}^1$ ,  $\text{CH}_2\text{SR}^1$  and  $\text{CH}_2\text{NR}^1\text{R}^2$ , wherein  $\text{R}^1$  and  $\text{R}^2$  are H,  $\text{C}_{1-4}$  alkyl or phenyl.

Typical optional substituents of phenyl moieties are fluorine, chlorine, methyl, methoxy, nitro and cyano.

The ring containing K, L and M in formula (I) is a pyrimidine ring which may be joined to the phenoxy groups by any two of its ring carbon atoms adjacent to a ring nitrogen atom. Of particular interest are those compounds of formula (I) in which K and L are both nitrogen and M is CH. Typically, one or both of X and Y are hydrogen. When one of X and Y is not hydrogen it is preferably attached to the 2-position of the phenyl ring.

Thus, in one aspect, the invention provides compounds of formula (I) in which K, L and M have the meanings previously given; X, which is preferably attached to the 2-position of the phenyl ring, is hydrogen, halogen (e.g. fluorine, chlorine or bromine),  $\text{C}_{1-4}$  alkyl (e.g. methyl or ethyl),  $\text{C}_{1-4}$  alkyl (especially methyl) substituted with halogen (e.g. fluorine, chlorine or bromine), hydroxy, cyano,  $\text{C}_{1-4}$  alkoxy (e.g. methoxy) or  $\text{C}_{1-4}$  alkanoyloxy (e.g. acetoxy),  $\text{C}_{2-4}$  alkenyl (e.g. ethenyl, allyl or methylallyl),  $\text{C}_{2-4}$  alkynyl (e.g. ethynyl or propargyl),  $\text{C}_{2-4}$  alkenyloxy (e.g. allyloxy),  $\text{C}_{2-4}$  alkynyloxy (e.g. propargyloxy), phenyl, benzyl, cyano, isocyano, thiocyanato, isothiocyanato, nitro, amino, mono- or  $\text{di}(\text{C}_{1-4})\text{alkylamino}$  (e.g. methylamino or dimethylamino), formylamino,  $\text{C}_{1-4}$  alkanoylamino (e.g. acetamido), benzoylamino, ureido, phenylureido,  $\text{C}_{1-4}$  alkylsulphonylamino (e.g. mesylamino), phenylsulphonylamino, hydroxy,  $\text{C}_{1-4}$  alkoxy (e.g. methoxy or ethoxy), phenoxy,  $\text{C}_{1-4}$  alkanoyloxy (e.g. acetoxy),  $\text{C}_{1-4}$  alkylsulphonyloxy (e.g. mesyloxy), phenylsulphonyloxy,  $\text{C}_{1-4}$  alkylthio (e.g. methylthio),  $\text{C}_{1-4}$  alkylsulphanyl (e.g. methylsulphanyl),  $\text{C}_{1-4}$  alkyl-

sulphonyl (e.g. mesyl or *n*-butylsulphonyl), formyl, C<sub>1-4</sub> alkanoyl (e.g. acetyl), benzoyl, hydroxyimino(C<sub>1-4</sub>)alkyl (e.g. hydroxyiminomethyl), C<sub>1-4</sub> alkoxyimino(C<sub>1-4</sub>)alkyl (e.g. methoxyiminomethyl), carbamoyl, C<sub>1-4</sub> alkylcarbamoyl (e.g. methylcarbamoyl), thiocarbamoyl or C<sub>1-4</sub> alkylthiocarbamoyl (e.g. methylthiocarbamoyl), the phenyl ring of any of the foregoing being optionally substituted with halogen (e.g. fluorine or chlorine), C<sub>1-4</sub> alkyl (e.g. methyl), C<sub>1-4</sub> alkoxy (e.g. methoxy), nitro or cyano; and Y is halogen (e.g. fluorine or chlorine), C<sub>1-4</sub> alkyl (e.g. methyl), C<sub>1-4</sub> alkoxy (e.g. methoxy), nitro, cyano or preferably, hydrogen, or X and Y, when ortho to one another, together form methylenedioxy, or together with the phenyl ring to which they are attached form a naphthalene, quinoline, benzimidazole or benzothienyl ring; and R<sup>3</sup> and R<sup>4</sup> are independently hydrogen or C<sub>1-4</sub> alkyl.

In another aspect the invention provides compounds of the formula (I.1), in which X is hydrogen, halogen (especially chlorine), C<sub>1-4</sub> alkyl (especially methyl), C<sub>1-4</sub> alkoxy (especially methoxy), trifluoromethyl, cyano, thiocarbamoyl or nitro; Y is hydrogen or fluoro; and R<sup>3</sup> and R<sup>4</sup> are independently hydrogen or C<sub>1-4</sub> alkyl.

The invention is illustrated by the compounds listed in Tables I to VI which follow. Compounds 1 to 160 in Table I have the general formula (I.2) in which X and Y have the values shown in that table. Compounds 161 to 200 in Table I have the general formula (I.3) in which Ar has the values shown in that table. The compounds in Tables II, III, IV, V and VI have the general formulae (I.4), (I.5), (I.6), (I.7) and (I.8), respectively, in which Z has the values shown in those tables. Throughout the tables the O-methyl oximinoacetamide group has the (E)-configuration, unless otherwise stated.

TABLE I

Compound No	X (see Formula (I.2))	Y	Compound No	X (see Formula (I.2))	Y
1	H	H	31	4-OCH <sub>3</sub>	H
2	2-F	H	32	2-OC <sub>2</sub> H <sub>5</sub>	H
3	3-F	H	33	3-(2-F-C <sub>6</sub> H <sub>4</sub> O)	H
4	4-F	H	34	2-OCOCH <sub>3</sub>	H
5	2-Cl	H	35	2-OSO <sub>2</sub> CH <sub>3</sub>	H
6	3-Cl	H	36	3-(4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> O)	H
7	4-Cl	H	37	2-thiocyanato	H
8	2-Br	H	38	3-thiocyanato	H
9A	2-Cyano	H	39	4-thiocyanato	H
9B <sup>+</sup>	2-Cyano	H	40	2-SCH <sub>3</sub>	H
10	3-Cyano	H	41	3-SCH <sub>3</sub>	H
11	4-Cyano	H	42	4-SCH <sub>3</sub>	H
12	2-Isocyano	H	43	2-S(O)CH <sub>3</sub>	H
13	2-NO <sub>2</sub>	H	44	2-SO <sub>2</sub> CH <sub>3</sub>	H
14	3-NO <sub>2</sub>	H	45	4-SO <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	H
15	4-NO <sub>2</sub>	H	46	2-CHO	H
16	2-NH <sub>2</sub>	H	47	3-CHO	H
17	3-NH(CH <sub>3</sub> )	H	48	4-CHO	H
18	2-N(CH <sub>3</sub> ) <sub>2</sub>	H	49	2-COCH <sub>3</sub>	H
19	2-NH.CHO	H	50	3-COC <sub>6</sub> H <sub>5</sub>	H
20	2-NH.COCH <sub>3</sub>	H	51	2-(E)-CH=NOH	H
21	3-NH.COC <sub>6</sub> H <sub>5</sub>	H	52	3-(E)-CH=NOH	H
22	2-NH.CONH <sub>2</sub>	H	53	4-(E)-CH=NOH	H
23	3-NH.CONH(C <sub>2</sub> H <sub>5</sub> )	H	54	2-(E)-CH=NOCH <sub>3</sub>	H
24	2-NH.SO <sub>2</sub> CH <sub>3</sub>	H	55	2-(E)-C(CH <sub>3</sub> )=NOH	H
25	3-NH.SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	H	56	2-CONH <sub>2</sub>	H
26	2-OH	H	57	3-CONH(CH <sub>3</sub> )	H
27	3-OH	H	58	4-CON(CH <sub>3</sub> ) <sub>2</sub>	H
28	4-OH	H	59	2-CSNH <sub>2</sub>	H
29	2-OCH <sub>3</sub>	H	60	2-CSNH(CH <sub>3</sub> )	H
30	2-O(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	H	61	2-CH <sub>3</sub>	H

TABLE I (Contd.)

Compound No	X (see Formula (I.2))	Y	Compound No	X (see Formula (I.2))	Y
62	3-CH <sub>3</sub>	H	93	2-OCH <sub>3</sub>	3-OCH <sub>3</sub>
63	4-CH <sub>3</sub>	H	94	2-Cyano	5-Cl
64	2-C <sub>2</sub> H <sub>5</sub>	H	95	2-Cyano	6-Cyano
65	2-CH <sub>2</sub> F	H	96	2-F	5-Cl
66	2-CH <sub>2</sub> Br	H	97	3-OCH <sub>3</sub>	5-OCH <sub>3</sub>
67	2-CH <sub>2</sub> Cl	H	98	3-Cyano	4-F
68	2-CH <sub>2</sub> CN	H	99	2-NO <sub>2</sub>	3-OCH <sub>3</sub>
69	2-CH <sub>2</sub> OH	H	100	3-OCH <sub>3</sub>	5-Cyano
70	2-CH <sub>2</sub> OCH <sub>3</sub>	H	101	2-CO <sub>2</sub> CH <sub>3</sub>	H
71	2-CH <sub>2</sub> OCOCH <sub>3</sub>	H	102	2-I	H
72	3-CH <sub>2</sub> CN	H	103	2-CF <sub>3</sub>	H
73	4-CH <sub>2</sub> OH	H	104	2- <u>i</u> -C <sub>3</sub> H <sub>7</sub>	H
74	3-CH <sub>2</sub> OCH <sub>3</sub>	H	105	2- <u>i</u> -C <sub>3</sub> H <sub>7</sub> O	H
75	2-CH=CH <sub>2</sub>	H	106	2-F	6-F
76	2-CH <sub>2</sub> CH=CH <sub>2</sub>	H	107	2-F	4-F
77	2-C≡CH	H	108	2-F	3-F
78	2-CH <sub>2</sub> C≡CH	H	109	2- <u>n</u> -C <sub>3</sub> H <sub>7</sub> O	H
79	3-CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub>	H	110	2- <u>n</u> -C <sub>4</sub> H <sub>9</sub> O	H
80	2-OCH <sub>2</sub> CH=CH <sub>2</sub>	H	111	2-CH(OH)CH <sub>3</sub>	H
81	2-OCH <sub>2</sub> C≡CH	H	112	2- <u>t</u> -C <sub>4</sub> H <sub>9</sub>	H
82	2-C <sub>6</sub> H <sub>5</sub>	H	113	2- <u>s</u> -C <sub>4</sub> H <sub>9</sub>	H
83	3-C <sub>6</sub> H <sub>5</sub>	H	114	2- <u>n</u> -C <sub>3</sub> H <sub>7</sub>	H
84	4-C <sub>6</sub> H <sub>5</sub>	H	115	2-( <u>E</u> )-CH=CH(CH <sub>3</sub> )	H
85	2-C <sub>6</sub> H <sub>5</sub> O	H	116	2-Cyano	4-OCH <sub>3</sub>
86	3-C <sub>6</sub> H <sub>5</sub> O	H	117	2-Cyano	5-OCH <sub>3</sub>
87	4-C <sub>6</sub> H <sub>5</sub> O	H	118	2-Cyano	4-Cl
88	2-(4-Cl-C <sub>6</sub> H <sub>4</sub> O)	H	119	2-Cyano	5-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>
89	2-C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O	H	120	2-CONH <sub>2</sub>	H
90	2-Cyano	4-Cl	121	2-C≡CSi(CH <sub>3</sub> ) <sub>3</sub>	H
91	2-NO <sub>2</sub>	4-F	122	2-F	5-F
92	2-Cl	4-Cl			

TABLE I (Contd.)

Compound No	X (see Formula (I.2))	Y	Compound No	X (see Formula (I.2))	Y
123	2-(E)- CH <sub>3</sub> O <sub>2</sub> C.C=NH.OCH <sub>3</sub>	H	152	2-Cyano	4-NO <sub>2</sub>
124	3-F	5-F	153	2-Cyano	6-NO <sub>2</sub>
125	2-NHOH	H	154	2-Cyano	6-OC <sub>2</sub> H <sub>5</sub>
126	2-CH <sub>2</sub> OCH <sub>3</sub>	H	155	2-Cyano	4-CO <sub>2</sub> CH <sub>3</sub>
127	2-CH <sub>2</sub> CN	H	156	2-Cyano	6-CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>
128	2-N <sub>3</sub>	H	157	2-Cyano	6-CH <sub>3</sub>
129	2-Cyano	6-F	158	2-Cyano	5-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>
130	2-NO <sub>2</sub>	6-F	159	2-Cyano	4-OCF <sub>3</sub>
131	2-CSNH <sub>2</sub>	6-F	160	2-Cyano	4-Cyano
132	2-Cyano	3-F			
133	2-Cyano	5-F			
134	2-Cyano	3-OCH <sub>3</sub>			
135	2-Cyano	6-OCH <sub>3</sub>			
136	2-NO <sub>2</sub>	4-OCH <sub>3</sub>			
137	2-NO <sub>2</sub>	5-OCH <sub>3</sub>			
138	2-NO <sub>2</sub>	6-OCH <sub>3</sub>			
139	2-CSNH <sub>2</sub>	3-OCH <sub>3</sub>			
140	2-CSNH <sub>2</sub>	4-OCH <sub>3</sub>			
141	2-CSNH <sub>2</sub>	5-OCH <sub>3</sub>			
142	2-CSNH <sub>2</sub>	6-OCH <sub>3</sub>			
143	2-Cyano	3-Cyano			
144	2-F	3-Cyano			
144	2-OCH <sub>3</sub>	3-Cyano			
145	3-Cyano	6-F			
146	*	H			
147	*	H			
148	*	H			
149	*	H			
150	2-Cyano	4-Br			
151	2-Cyano	6-Br			
			Compound No	Ar (see Formula (I.3))	
			161	*	
			162	*	
			163	*	
			164	*	
			165	*	
			166	*	
			167	Pentafluorophenyl	
			168	2,4,6-Tri-F-C <sub>6</sub> H <sub>2</sub>	
			169	2,3,5,6-Tetra-F-C <sub>6</sub> H	
			170	2,3,6-Tri-F-C <sub>6</sub> H <sub>2</sub>	
			171	2,3-Di-cyano-6-F-C <sub>6</sub> H <sub>2</sub>	
			172	2,6-Di-F-3-CH <sub>3</sub> O-C <sub>6</sub> H <sub>2</sub>	
			173	2,6-Di-F-4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>2</sub>	
			174	2,6-Di-F-3-NO <sub>2</sub> -C <sub>6</sub> H <sub>2</sub>	
			175	2,6-Di-F-4-NO <sub>2</sub> -C <sub>6</sub> H <sub>2</sub>	
			177	4,6-Di-Br-2-cyano-C <sub>6</sub> H <sub>2</sub>	
			176	2,6-Di-F-3,5-di-CH <sub>3</sub> O-C <sub>6</sub> H	
			178	3-Cyano-2,6-di-F-C <sub>6</sub> H <sub>2</sub>	

TABLE I (Contd.)

Compound No	Ar (see Formula (I.3))	Compound No	Ar (see Formula I.3))
179	6-Br-2-cyano-4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>2</sub>	190	2-Cyano-4,6-di-NO <sub>2</sub> -C <sub>6</sub> H <sub>2</sub>
180	6-Br-4-Cl-2-cyano-C <sub>6</sub> H <sub>2</sub>	191	2-Cyano-4-CH <sub>3</sub> -6-NO <sub>2</sub> -C <sub>6</sub> H <sub>2</sub>
181	6-Br-2-cyano-4-NO <sub>2</sub> -C <sub>6</sub> H <sub>2</sub>	192	2-Cyano-4-CH <sub>3</sub> O-6-NO <sub>2</sub> -C <sub>6</sub> H <sub>2</sub>
182	3-Br-2-cyano-6-CH <sub>3</sub> O-C <sub>6</sub> H <sub>2</sub>	193	2-Cyano-5,6-di-CH <sub>3</sub> O-C <sub>6</sub> H <sub>2</sub>
183	3,5-Di-Cl-2-cyano-C <sub>6</sub> H <sub>2</sub>	194	2-Cyano-5,6-di-CH <sub>3</sub> O-3-CH <sub>3</sub> -C <sub>6</sub> H
184	4,6-Di-Cl-2-cyano-C <sub>6</sub> H <sub>2</sub>	195	3,4-Di-Br-2-cyano-6-CH <sub>3</sub> O-C <sub>6</sub> H
185	3-Br-2-cyano-4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>2</sub>	196	3-Br-2-cyano-6-CH <sub>3</sub> O-4-NO <sub>2</sub> -C <sub>6</sub> H
186	4-Br-2-cyano-6-NO <sub>2</sub> -C <sub>6</sub> H <sub>2</sub>	197	2-Cyano-6-CH <sub>3</sub> CH <sub>2</sub> O-4-NO <sub>2</sub> -C <sub>6</sub> H <sub>2</sub>
187	4-Br-2-cyano-6-CH <sub>3</sub> O-C <sub>6</sub> H <sub>2</sub>	198	*
188	2-Cyano-4-I-6-CH <sub>3</sub> O-C <sub>6</sub> H <sub>2</sub>	199	*
189	2-Cyano-6-CH <sub>3</sub> O-4-NO <sub>2</sub> -C <sub>6</sub> H <sub>2</sub>	200	2-Cyano-3,4-di-CH <sub>3</sub> -C <sub>6</sub> H <sub>2</sub>

\* These values are given later under "Chemical Formulae".

+ The O-methyl oxyiminoacetamide group has the (Z)-configuration.

TABLE II

Table II comprises 200 compounds of the general formula (I.4) wherein Z is X-Y-C<sub>6</sub>H<sub>3</sub> or Ar which have all the values listed in Table I. That is, compounds numbers 1 to 200 of Table II are the same as those of Table I except that the compounds of Table I have an N-methyl substituent on the acetamide group whereas the compounds of Table II have not.

TABLE III

Table III comprises 200 compounds of the general formula (I.5) wherein Z is X-Y-C<sub>6</sub>H<sub>3</sub> or Ar which have all the values listed in Table I. That is, compounds numbers 1 to 200 of Table III are the same as those of Table I except that the pyrimidine ring is 4,6-disubstituted in Table I and 2,4-disubstituted as shown in Table III.

TABLE IV

Table IV comprises 200 compounds of the general formula (I.6) wherein Z is X-Y-C<sub>6</sub>H<sub>3</sub> or Ar which have all the values listed in Table I. That is, compounds numbers 1 to 200 of Table IV are the same as those of Table II except that the pyrimidine ring is 4,6-disubstituted in Table I and 2,4-disubstituted as shown in Table IV.



TABLE V

Table V comprises 200 compounds of the general formula (I.7) wherein Z is  $X-Y-C_6H_3$  or Ar which have all the values listed in Table I. That is, compounds numbers 1 to 200 of Table V are the same as those of Table I except that the pyrimidine ring is 4,6-disubstituted in Table I and 2,4-disubstituted as shown in Table V, and the compounds of Table I have an N-methyl substituent on the acetamide group whereas the compounds of Table V have not.

TABLE VI

Table VI comprises 200 compounds of the general formula (I.8) wherein Z is  $X-Y-C_6H_3$  or Ar which have all the values listed in Table I. That is, compounds numbers 1 to 200 of Table VI are the same as those of Table I except that the pyrimidine ring is 4,6-disubstituted in Table I and 2,4-disubstituted as shown in Table VI, and the compounds of Table I have an N-methyl substituent on the acetamide group whereas the compounds of Table VI have not.

The compounds of the invention can be prepared according to the methods described in EP-A-0382375 and EP-A-0398692. The former reference shows how to prepare similar compounds, but which have a methyl  $\beta$ -methoxyacrylate group attached to the phenyl ring in formula I instead of an O-methyl oxyiminoacetamide group. The latter reference shows how to construct the oxyiminoacetamide group.

The compounds of the invention are active fungicides and may be used to control one or more of the following pathogens:  
Pyricularia oryzae on rice. Puccinia recondita, Puccinia striiformis and other rusts on wheat, Puccinia hordei, Puccinia striiformis and other rusts on barley, and rusts on other hosts e.g. coffee, pears, apples, peanuts, vegetables and ornamental plants. Erysiphe graminis (powdery mildew) on barley and wheat and other powdery mildews on various hosts such as Sphaerotheca macularis on hops, Sphaerotheca fuliginea on cucurbits (e.g. cucumber), Podosphaera leucotricha on apple and Uncinula necator on vines. Helminthosporium spp., Rhynchosporium spp., Septoria spp., Pyrenophora spp., Pseudocercospora herpotrichoides and Gaeumannomyces graminis on cereals. Cercospora arachidicola and Cercosporidium personata on peanuts and other Cercospora species on other hosts, for example, sugar beet, bananas, soya beans and rice. Botrytis cinerea (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts. Alternaria spp. on vegetables (e.g. cucumber), oil-seed rape, apples, tomatoes and other

hosts. Venturia inaequalis (scab) on apples. Plasmopara viticola on vines. Other downy mildews such as Bremia lactucae on lettuce, Peronospora spp. on soybeans, tobacco, onions and other hosts, Pseudoperonospora humuli on hops and Pseudoperonospora cubensis on cucurbits. Phytophthora infestans on potatoes and tomatoes and other Phytophthora spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco, cocoa and other hosts. Thanatephorus cucumeris on rice and other Rhizoctonia species on various hosts such as wheat and barley, vegetables, cotton and turf.

Some of the compounds show a broad range of activities against fungi in vitro. They may also have activity against various post-harvest diseases of fruit (e.g. Penicillium digitatum and italicum and Trichoderma viride on oranges, Gloeosporium musarum on bananas and Botrytis cinerea on grapes).

Further, some of the compounds may be active as seed dressings against pathogens including Fusarium spp., Septoria spp., Tilletia spp., (bunt, a seed-borne disease of wheat), Ustilago spp. and Helminthosporium spp. on cereals, Rhizoctonia solani on cotton and Pyricularia oryzae on rice.

The compounds may move acropetally/locally in plant tissue. Moreover, the compounds may be volatile enough to be active in the vapour phase against fungi on the plant.

The invention therefore provides a method of combating fungi which comprises applying to a plant, to a seed of a plant or to the locus of the plant or seed a fungicidally effective amount of a compound as hereinbefore defined, or a composition containing the same.

The compounds may be used directly for agricultural purposes but are more conveniently formulated into compositions using a carrier or diluent. The invention thus provides fungicidal compositions comprising a compound as hereinbefore defined and an acceptable carrier or diluent therefor.

The compounds can be applied in a number of ways. For example, they can be applied, formulated or unformulated, directly to the foliage of a plant, to seeds or to other medium in which plants are growing or are to be planted, or they can be sprayed on, dusted on or applied as a cream or paste formulation, or they can be applied as a vapour or as slow release granules.

Application can be to any part of the plant including the foliage, stems, branches or roots, or to soil surrounding the roots, or to the seed before it is planted, or to the soil generally, to paddy water or to hydroponic culture systems. The invention compounds may also be injected

into plants or sprayed onto vegetation using electrodynamic spraying techniques or other low volume methods.

The term "plant" as used herein includes seedlings, bushes and trees. Furthermore, the fungicidal method of the invention includes preventative, protectant, prophylactic and eradicant treatments.

The compounds are preferably used for agricultural and horticultural purposes in the form of a composition. The type of composition used in any instance will depend upon the particular purpose envisaged.

The compositions may be in the form of dustable powders or granules comprising the active ingredient (invention compound) and a solid diluent or carrier, for example, fillers such as kaolin, bentonite, kieselguhr, dolomite, calcium carbonate, talc, powdered magnesia, fuller's earth, gypsum, diatomaceous earth and china clay. Such granules can be preformed granules suitable for application to the soil without further treatment. These granules can be made either by impregnating pellets of filler with the active ingredient or by pelleting a mixture of the active ingredient and powdered filler. Compositions for dressing seed may include an agent (for example, a mineral oil) for assisting the adhesion of the composition to the seed; alternatively the active ingredient can be formulated for seed dressing purposes using an organic solvent (for example, N-methylpyrrolidone, propylene glycol or dimethylformamide). The compositions may also be in the form of wettable powders or water dispersible granules comprising wetting or dispersing agents to facilitate the dispersion in liquids. The powders and granules may also contain fillers and suspending agents.

Emulsifiable concentrates or emulsions may be prepared by dissolving the active ingredient in an organic solvent optionally containing a wetting or emulsifying agent and then adding the mixture to water which may also contain a wetting or emulsifying agent. Suitable organic solvents are aromatic solvents such as alkylbenzenes and alkylnaphthalenes, ketones such as cyclohexanone and methylcyclohexanone, chlorinated hydrocarbons such as chlorobenzene and trichlorethane, and alcohols such as benzyl alcohol, furfuryl alcohol, butanol and glycol ethers.

Suspension concentrates of largely insoluble solids may be prepared by ball or bead milling with a dispersing agent with a suspending agent included to stop the solid settling.

Compositions to be used as sprays may be in the form of aerosols wherein the formulation is held in a container under pressure of a propellant, e.g. fluorotrichloromethane or dichlorodifluoromethane.

The invention compounds can be mixed in the dry state with a pyrotechnic mixture to form a composition suitable for generating in enclosed spaces a smoke containing the compounds.

Alternatively, the compounds may be used in micro-encapsulated form. They may also be formulated in biodegradable polymeric formulations to obtain a slow, controlled release of the active substance.

By including suitable additives, for example additives for improving the distribution, adhesive power and resistance to rain on treated surfaces, the different compositions can be better adapted for various utilities.

The invention compounds can be used as mixtures with fertilisers (e.g. nitrogen-, potassium- or phosphorus-containing fertilisers). Compositions comprising only granules of fertiliser incorporating, for example coated with, the compound are preferred. Such granules suitably contain up to 25% by weight of the compound. The invention therefore also provides a fertiliser composition comprising a fertiliser and the compound of general formula (I) or a salt or metal complex thereof.

Wettable powders, emulsifiable concentrates and suspension concentrates will normally contain surfactants, e.g. a wetting agent, dispersing agent, emulsifying agent or suspending agent. These agents can be cationic, anionic or non-ionic agents.

Suitable cationic agents are quaternary ammonium compounds, for example, cetyltrimethylammonium bromide. Suitable anionic agents are soaps, salts of aliphatic monoesters of sulphuric acid (for example, sodium lauryl sulphate), and salts of sulphonated aromatic compounds (for example, sodium dodecylbenzenesulphonate, sodium, calcium or ammonium lignosulphonate, butylnaphthalene sulphonate, and a mixture of sodium diisopropyl- and triisopropyl- naphthalene sulphonates).

Suitable non-ionic agents are the condensation products of ethylene oxide with fatty alcohols such as oleyl or cetyl alcohol, or with alkyl phenols such as octyl- or nonylphenol and octylcresol. Other non-ionic agents are the partial esters derived from long chain fatty acids and hexitol anhydrides, the condensation products of the said partial esters with ethylene oxide, and the lecithins. Suitable suspending agents are hydrophilic colloids (for example, polyvinylpyrrolidone and sodium carboxymethylcellulose), and swelling clays such as bentonite or attapulgite.

Compositions for use as aqueous dispersions or emulsions are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, the concentrate being diluted with water before use. These concentrates should preferably be able to withstand storage for prolonged periods and after such storage be capable of dilution with water in order to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. The concentrates may conveniently contain up to 95%, suitably 10-85%, for example 25-60%, by weight of the active ingredient. After dilution to form aqueous preparations, such preparations may contain varying amounts of the active ingredient depending upon the intended purpose, but an aqueous preparation containing 0.0005% or 0.01% to 10% by weight of active ingredient may be used.

The compositions of this invention may contain other compounds having biological activity, e.g. compounds having similar or complementary fungicidal activity or which possess plant growth regulating, herbicidal or insecticidal activity.

A fungicidal compound which may be present in the composition of the invention may be one which is capable of combating ear diseases of cereals (e.g. wheat) such as Septoria, Gibberella and Helminthosporium spp., seed and soil-borne diseases and downy and powdery mildews on grapes and powdery mildew and scab on apple, etc. By including another fungicide, the composition can have a broader spectrum of activity than the compound of general formula (I) alone. Further the other fungicide can have a synergistic effect on the fungicidal activity of the compound of general formula (I). Examples of fungicidal compounds which may be included in the composition of the invention are (RS)-1-aminopropylphosphonic acid, (RS)-4-(4-chlorophenyl)-2-phenyl-2-(1H-1,2,4-triazol-1-yl-methyl)butyronitrile, (Z)-N-but-2-enyloxymethyl-2-chloro-2',6'-diethylacetanilide, 1-(2-cyano-2-methoxyimino-acetyl)-3-ethyl urea, 1-[(2RS,4RS;2RS,4RS)-4-bromo-2-(2,4-dichlorophenyl)tetrahydrofurfuryl]-1H-1,2,4-triazole, 3-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-quinazolin-4(3H)-one, 3-chloro-4-[4-methyl-2-(1H-1,2,4-triazol-1-yl-methyl)-1,3-dioxolan-2-yl]-phenyl-4-chlorophenyl ether, 4-bromo-2-cyano-N,N-dimethyl-6-trifluoromethylbenzimidazole-1-sulphonamide, 5-ethyl-5,8-dihydro-8-oxo(1,3)-dioxolo(4,5-g)quinoline-7-carboxylic acid,  $\alpha$ -[N-(3-chloro-2,6-xylyl)-2-methoxyacetamido]- $\gamma$ -butyrolactone, aldimorph, anilazine, benalaxyl, benomyl, biloxazol, binapacryl, bitertanol, blasticidin S, bupirimate,

buthiobate, captafol, captan, carbendazim, carboxin, chlorbenz-thiazone, chloroneb, chlorothalonil, chlorozolinate, copper containing compounds such as copper oxychloride, copper sulphate and Bordeaux mixture, cycloheximide, cymoxanil, cyproconazole, cyprofuram, di-2-pyridyl disulphide 1,1'-dioxide, dichlofluanid, dichlone, diclobutrazol, diclomezine, dicloran, difenoconazole, dimethamorph, dimethirimol, diniconazole, dinocap, ditalimfos, dithianon, dodemorph, dodine, edifenphos, etaconazole, ethirimol, ethyl (Z)-N-benzyl-N-([methyl(methylthioethylideneamino-oxy-carbonyl)amino]thio)- $\beta$ -alaninate, etridiazole, fenapanil, fenarimol, fenfuram, fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, flutolanil, flutriafol, flusilazole, folpet, fosetyl-aluminium, fuberidazole, furalaxyl, furconazole-cis, guazatine, hexaconazole, hydroxyisoxazole, imazalil, imibenconazole, iprobenfos, iprodione, isoprothiolane, kasugamycin, mancozeb, maneb, mepanipyrim, mepronil, metalaxyl, methfuroxam, metsulfovax, myclobutanil, N-(4-methyl-6-prop-1-ynylpyrimidin-2-yl)aniline, neoasozin, nickel dimethyldithiocarbamate, nitrothal-isopropyl, nuarimol, ofurace, organomercury compounds, oxadixyl, oxycarboxin, pefurazoate, penconazole, pencycuron, phenazin oxide, phthalide, polyoxin D, polyram, probenazole, prochloraz, procymidone, propamocarb, propiconazole, propineb, prothiocarb, pyrazophos, pyrifenox, pyroquilon, pyroxyfur, pyrrolnitrin, quinomethionate, quintozone, SSF-109, streptomycin, sulphur, tebuconazole, techlofthalam, tecnazene, tetraconazole, thiabendazole, thicyofen, thiophanate-methyl, thiram, tolclofos-methyl, triacetate salt of 1,1'-iminodi(octamethylene)-diguanidine, triadimefon, triadimenol, triazbutyl, tricyclazole, tridemorph, triforine, validamycin A, vinclozolin, zarilamid and zineb. The compounds of general formula (I) can be mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar fungal diseases.

Suitable insecticides which may be incorporated in the composition of the invention include buprofezin, carbaryl, carbofuran, carbosulfan, chlorpyrifos, cycloprothrin, demeton-s-methyl, diazinon, dimethoate, ethofenprox, fenitrothion, fenobucarb, fenthion, formothion, isoprocab, isoxathion, monocrotophos, phenthoate, pirimicarb, propaphos and XMC.

Plant growth regulating compounds are compounds which control weeds or seedhead, formation, or selectively control the growth of less desirable plants (e.g. grasses).

Examples of suitable plant growth regulating compounds for use with the invention compounds are 3,6-dichloropicolinic acid, 1-(4-chlorophenyl)-4,6-di-methyl-2-oxo-1,2-dihydropyridine-3-carboxylic acid, methyl-3,6-dichloroanisate, abscisic acid, asulam, benzoylprop-ethyl, carbetamide, daminozide, difenzoquat, dikegulac, ethephon, fenpentezol, fluoridamid, glyphosate, glyphosine, hydroxybenzonitriles (e.g. bromoxynil), inabenfide, isopyrimol, long chain fatty alcohols and acids, maleic hydrazide, mefluidide, morphactins (e.g. chlorfluoroecol), paclobutrazol, phenoxyacetic acids (e.g. 2,4-D or MCPA), substituted benzoic acid (e.g. triiodo-benzoic acid), substituted quaternary ammonium and phosphonium compounds (e.g. chloromequat, chlorphonium or mepiquatchloride), tecnazene, the auxins (e.g. indoleacetic acid, indolebutyric acid, naphthylacetic acid or naphthoxyacetic acid), the cytokinins (e.g. benzimidazole, benzyladenine, benzylaminopurine, diphenylurea or kinetin), the gibberellins (e.g. GA<sub>3</sub>, GA<sub>4</sub> or GA<sub>7</sub>) and triapenthenol.

The following Examples illustrate the invention. In the Examples, the term 'ether' refers to diethyl ether, anhydrous magnesium sulphate was used to dry solutions, and solutions were concentrated under reduced pressure. Reactions involving air- or water-sensitive intermediates were performed under an atmosphere of nitrogen and solvents were dried before use, where appropriate. Unless otherwise stated, chromatography was performed on a column of silica gel as the stationary phase. NMR data are selective; no attempt is made to list every absorption in all cases. <sup>1</sup>H NMR spectra were recorded using CDCl<sub>3</sub>-solutions on an instrument operating at 270 MHz, unless otherwise stated. The following abbreviations are used :

NMR	= nuclear magnetic resonance	br	= broad
MS	= mass spectrum	s	= singlet
IR	= infrared	d	= doublet
q	= quartet	m	= multiplet
dd	= doublet of doublets	mp	= melting point
ppm	= parts per million	CI	= chemical ionisation
EI	= electron ionisation		

EXAMPLE 1

This Example illustrates the preparation of the carboxamide (A) (see under "Chemical Formulae") and the corresponding (Z)-isomer (Compounds Nos. 9A and 9B of Table I).

To a vigorously stirred mixture of water (20ml) and a solution of (E)-methyl 2-[2-(6-(2-cyanophenoxy)pyrimidin-4-yloxy)phenyl]-3-methoxypropenoate (3.2g, 7.94 mmol, prepared as described in Example 3 of EP-A-0 382 375) in dichloromethane (20ml) was added potassium permanganate (2.5g, 15.9 mmol) in one portion and tetra-n-hexylammonium hydrogen sulphate (200mg). The reaction mixture was stirred overnight (16 hours) and then filtered. The filter was washed through with ether and water and then the combined liquid phases were extracted with ether (x3). The ether extracts were washed with water (x3) and brine (x1), dried, filtered and evaporated. The residue was chromatographed (eluent dichloromethane-acetone, 98:2). Recrystallisation (ether-pentane) of the major component afforded methyl 2-[2-(6-(2-cyanophenoxy)pyrimidin-4-yloxy)phenyl]ketoacetate (2.105g, 71%) as a white crystalline solid, mp 96-97°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.83(3H,s), 6.61(1H,s), 7.27-7.47(4H,m), 7.67-7.76(3H,m), 8.02(1H,dd), 8.39(1H,s) ppm; IR maxima 2234(CN), 1743(CO, ester), 1688(CO, ketone)cm<sup>-1</sup>.

To a solution of the ketoester (500mg, 1.33 mmol) in dry methanol (10ml) was added methoxylamine hydrochloride (112mg, 1.33 mmol). After stirring at room temperature for 4 hours, more methoxylamine hydrochloride (66mg) was added and stirring was continued overnight. The complete disappearance of the starting ketoester was demonstrated by loss of the peak at 1688 cm<sup>-1</sup> in the infrared spectrum. The reaction mixture was worked up and then repeatedly chromatographed (eluent dichloromethane-acetone mixtures) to afford, in order of increasing polarity, (Z)-methyl O-methyl-2-[2-(6-(2-cyanophenoxy)pyrimidin-4-yloxy)phenyl]oxyiminoacetate as a white foam (75mg, 14%); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.78(3H,s), 3.98(3H,s), 6.50(1H,s), 7.18(1H,d), 7.31-7.41(3H,m), 7.48-7.54(1H,m), 7.66-7.81(3H,m), 8.38(1H,s) ppm; IR maxima 2242 (CN), 1741(CO) cm<sup>-1</sup>; MS (EI) 404 (M<sup>+</sup>) and (CI) 422 (M+ NH<sub>4</sub><sup>+</sup>), 405 (MH<sup>+</sup>); and (E)-methyl O-methyl-2-[2-(6-(2-cyanophenoxy)pyrimidin-4-yloxy)phenyl]oxyiminoacetate as an off-white solid (403mg, 75%), mp 125-127°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.81(3H,s), 3.94(3H,s), 6.51(1H,s), 7.27-7.43(4H,m), 7.49-7.55(1H,m), 7.65-7.73(3H,m), 8.39(1H,s) ppm; IR maxima 2234 (CN), 1728 (CO) cm<sup>-1</sup>; MS (EI) 404 (M<sup>+</sup>); (CI) 422 (M+ NH<sub>4</sub><sup>+</sup>), 405 (MH<sup>+</sup>).



(E)-Methyl O-methyl-2-[2-(6-(2-cyanophenoxy)pyrimidin-4-yloxy)phenyl]-oxyiminoacetate (403 mg) was dissolved in a solution of methylamine in industrial methylated spirits (0.5ml, ca. 33% w/w) and the resulting mixture was stirred at room temperature for 8 hours, then allowed to stand overnight. The mixture was poured into water and extracted with ether. The extracts were washed with water, dried, concentrated and then chromatographed twice using first ether and then 10% acetone in dichloromethane as eluants to give, in order of increasing polarity, the title compound (A) (295mg, 73% yield) as a clear gum which crystallised from a mixture of ether and pentane to give a white solid, mp 146-7°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.88(3H,d), 3.82(3H,s), 6.52(1H,s), 6.70(1H,br q), 7.24-7.53(6H,m), 7.70(2H,m), 8.38(1H,s) ppm; IR maxima 3381, 2234, 1671, 1563  $\text{cm}^{-1}$ ; MS (EI) 403 ( $\text{M}^+$ ) and (CI) 404 ( $\text{MH}^+$ ), 421 ( $\text{M}+\text{NH}_4^+$ ); and 4-(2-cyanophenoxy)-6-methylaminopyrimidine (22mg) as an off-white solid, mp 152-3°C.

Under similar conditions (3.5 hours reaction time), (Z)-methyl O-methyl-2-[2-(6-(2-cyanophenoxy)pyrimidin-4-yloxy)phenyl]oxyiminoacetate gave the (Z)-isomer corresponding to (A) (65% yield) as a clear gum,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.87(3H,d), 3.94(3H,s), 6.42(1H, br q), 6.52(1H,s), 7.20(1H,d), 7.35(3H,m), 7.50(1H,m), 7.70(3H,m), 8.38(1H,s) ppm; MS (EI) 403 ( $\text{M}^+$ ).

The following are examples of compositions suitable for agricultural and horticultural purposes which can be formulated from the compounds of the invention. Such compositions form another aspect of the invention. Percentages are by weight.

#### EXAMPLE 2

An emulsifiable concentrate is made up by mixing and stirring the ingredients until all are dissolved.

Compound No. 9A of Table I	10%
Benzyl alcohol	30%
Calcium dodecylbenzenesulphonate	5%
Nonylphenoethoxylate (13 mole ethylene oxide)	10%
Alkyl benzenes	45%

#### EXAMPLE 3

The active ingredient is dissolved in methylene dichloride and the resultant liquid sprayed on to the granules of attapulgite clay. The solvent is then allowed to evaporate to produce a granular composition.

Compound No. 9A of Table I	5%
Attapulgate granules	95%

EXAMPLE 4

A composition suitable for use as a seed dressing is prepared by grinding and mixing the three ingredients.

Compound No. 9A of Table I	50%
Mineral oil	2%
China clay	48%

EXAMPLE 5

A dustable powder is prepared by grinding and mixing the active ingredient with talc.

Compound No. 9A of Table I	5%
Talc	95%

EXAMPLE 6

A suspension concentrate is prepared by ball milling the ingredients to form an aqueous suspension of the ground mixture with water.

Compound No. 9A of Table I	40%
Sodium lignosulphonate	10%
Bentonite clay	1%
Water	49%

This formulation can be used as a spray by diluting into water or applied directly to seed.

EXAMPLE 7

A wettable powder formulation is made by mixing together and grinding the ingredients until all are thoroughly mixed.

Compound No. 6 of Table I	25%
Sodium lauryl sulphate	2%
Sodium lignosulphonate	5%
Silica	25%
China clay	43%

EXAMPLE 8

The compounds were tested against a variety of foliar fungal diseases of plants. The technique employed was as follows.

The plants were grown in John Innes Potting Compost (No 1 or 2) in 4 cm diameter minipots. The test compounds were formulated either by bead milling with aqueous Dispersol T or as a solution in acetone or acetone/ethanol which was diluted to the required concentration immediately

before use. The formulations (100 ppm active ingredient) were sprayed on to the foliage or applied to the roots of the plants in the soil. The sprays were applied to maximum retention and the root drenches to a final concentration equivalent to approximately 40 ppm a.i. in dry soil. Tween 20 was added to give a final concentration of 0.05% when the sprays were applied to cereals.

For most of the tests the compounds were applied to the soil (roots) or to the foliage (by spraying) one or two days before the plant was inoculated with the disease. An exception was the test on Erysiphe graminis in which the plants were inoculated 24 hours before treatment. Foliar pathogens were applied by spray as zoosporangial suspensions onto the leaves of test plants. After inoculation, the plants were put into an appropriate environment to allow infection to proceed and then incubated until the disease was ready for assessment. The period between inoculation and assessment varied from four to fourteen days according to the disease and environment.

The disease level present (i.e. leaf area covered by actively sporulating disease) on each of the treated plants was recorded using the following assessment scale:

0 = 0% disease present	20 = 10.1-20% disease present
1 = 0.1-1% disease present	30 = 20.1-30% disease present
3 = 1.1-3% disease present	60 = 30.1-60% disease present
5 = 3.1-5% disease present	90 = 60.1-100% disease present
10 = 5.1-10% disease present	

Each assessment was then expressed as a percentage of the level of disease present on the untreated control plants. This calculated value is referred to as a POCO (Percentage of Control) value. An example of a typical calculation is as follows:

Disease level on untreated control = 90

Disease level on treated plant = 30

$$\text{POCO} = \frac{\text{disease level on treated plant}}{\text{disease level on untreated control}} \times 100 = \frac{30}{90} \times 100 = 33.3$$

This calculated POCO value is then rounded to the nearest of the values in the 9-point assessment scale shown above. In this particular example, the POCO value would be rounded to 30. If the calculated POCO

falls exactly mid-way between two of the points, it is rounded to the lower of the two values.

The results displayed in Table III below represent these rounded POCO values.

TABLE III

Compound No of Table I	Pr	Egt	Sn	Po	Tc	Vi	Pv	Pil
9A	0	0	0	0	0	0	0	0
9B	90 <sup>a</sup>	20 <sup>a</sup>	90 <sup>a</sup>	60 <sup>a</sup>	90 <sup>a</sup>	60 <sup>a</sup>	90 <sup>a</sup>	90 <sup>a</sup>

a = 10 ppm foliar spray only.

Key to diseases

Pr Puccinia recondita  
Egt Erysiphe graminis tritici  
Sn Septoria nodorum  
Po Pyricularia oryzae  
Tc Thanetophorus cucumeris  
Vi Venturia inaequalis  
Pv Plasmopara viticola  
Pil Phytophthora infestans lycopersici

CHEMICAL FORMULAE  
(in description)

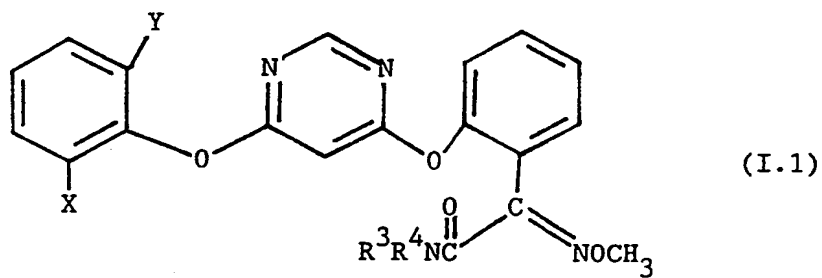
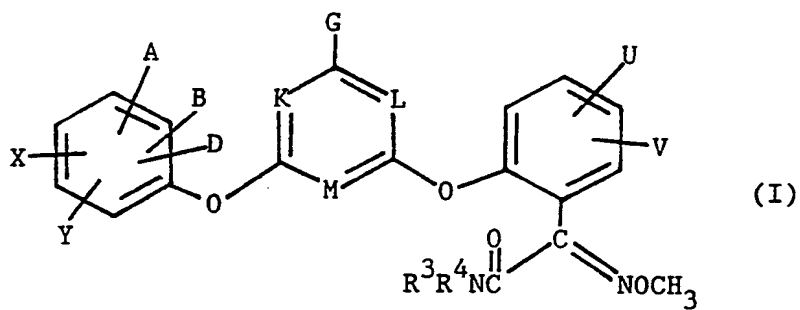
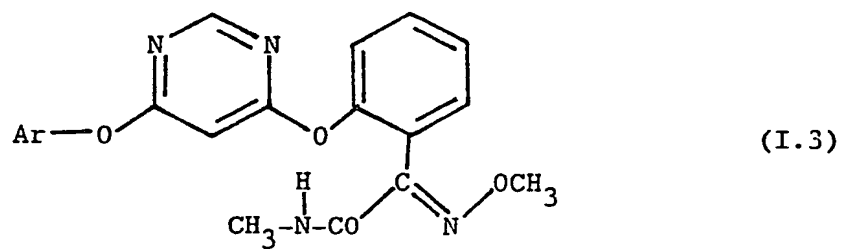
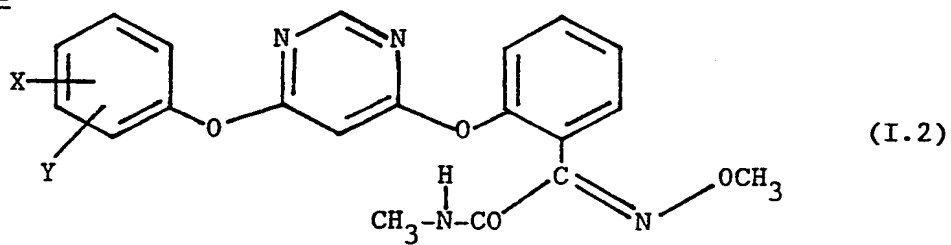
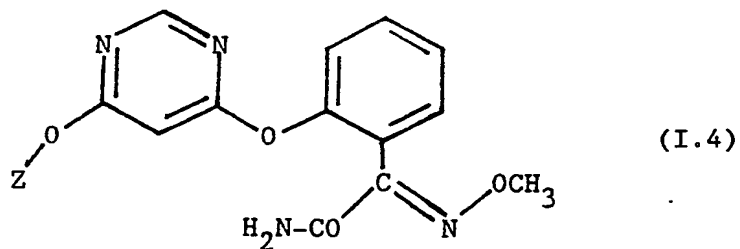
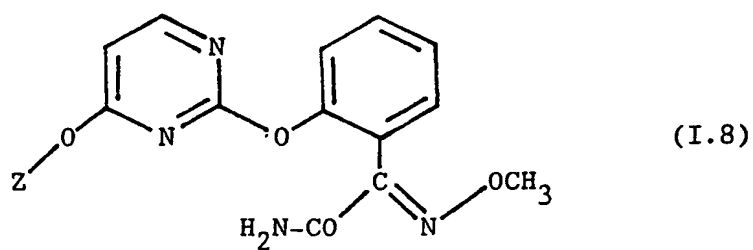
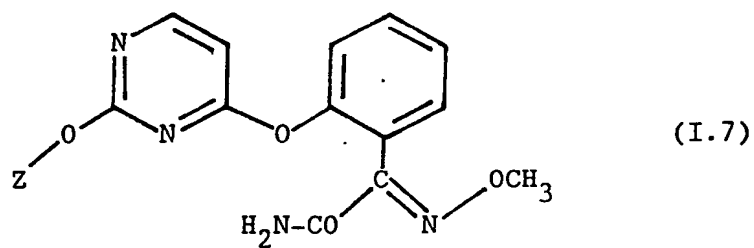
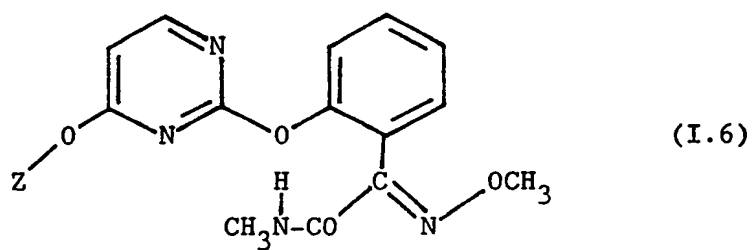
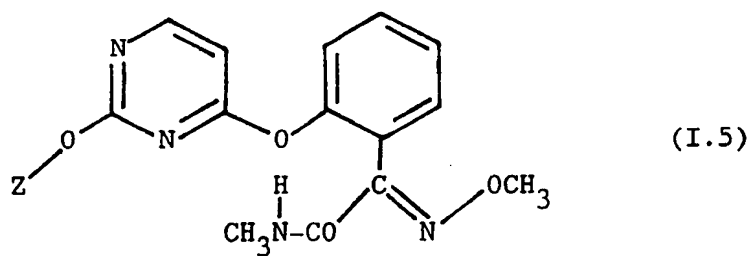


TABLE I

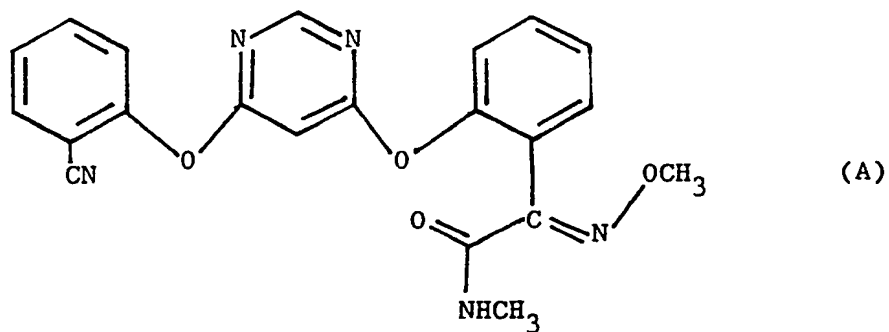


TABLES II TO IV



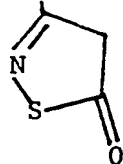


EXAMPLE 1

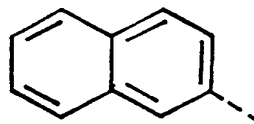


\* X of Compound No 146 is

2-

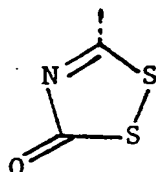


\* Ar of Compound No 163 is

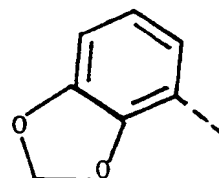


\* X of Compound No 147 is

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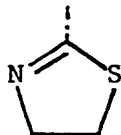


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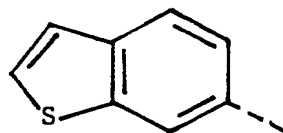


\* X of Compound No 148 is

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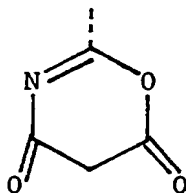


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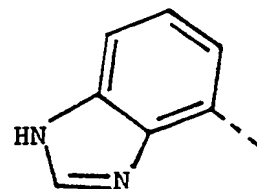


\* X of Compound No 149 is

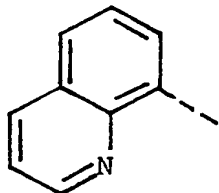
2-



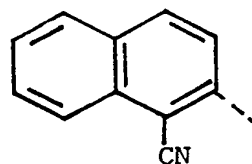
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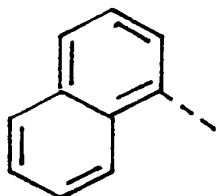
\* Ar of Compound No 161 is



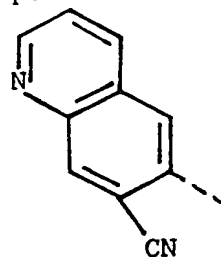
\* Ar of Compound No 198 is



\* Ar of Compound No 162 is

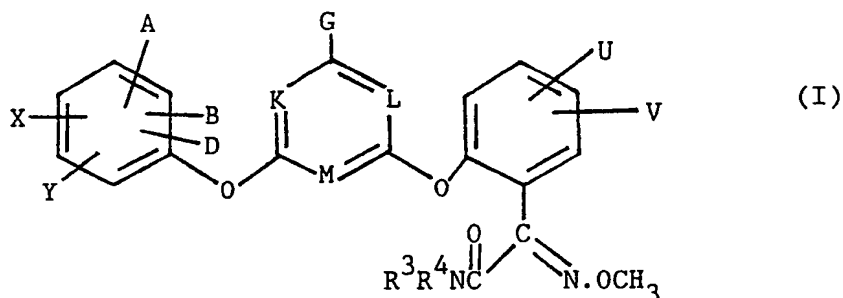


\* Ar of Compound No 199 is



CLAIMS

1. A compound having the formula (I):



in which any two of K, L and M are nitrogen and the other is CE; X and Y are independently hydrogen, halogen, C<sub>1-4</sub> alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>2-8</sub> alkenyl, C<sub>2-8</sub> alkynyl, C<sub>2-4</sub> alkynyloxy, phenyl, benzyloxy, cyano, isocyano, isothiocyanato, nitro, NR<sup>1</sup>R<sup>2</sup>, NR<sup>1</sup>OR<sup>2</sup>, N<sub>3</sub>, NHCOR<sup>1</sup>, NR<sup>1</sup>CO<sub>2</sub>R<sup>2</sup>, NHCONR<sup>1</sup>R<sup>2</sup>, N=CHNR<sup>1</sup>R<sup>2</sup>, NHSO<sub>2</sub>R<sup>1</sup>, OR<sup>1</sup>, OCOR<sup>1</sup>, OSO<sub>2</sub>R<sup>1</sup>, SR<sup>1</sup>, SOR<sup>1</sup>, SO<sub>2</sub>R<sup>1</sup>, SO<sub>2</sub>OR<sup>1</sup>, SO<sub>2</sub>NR<sup>1</sup>R<sup>2</sup>, COR<sup>1</sup>, CR<sup>1</sup>=NOR<sup>2</sup>, CHR<sup>1</sup>CO<sub>2</sub>R<sup>2</sup>, CO<sub>2</sub>R<sup>1</sup>, CONR<sup>1</sup>R<sup>2</sup>, CSNR<sup>1</sup>R<sup>2</sup>, CH<sub>3</sub>O<sub>2</sub>C.C:CH.OCH<sub>3</sub>, 1-(imidazol-1-yl), vinyl, a 5-membered heterocyclic ring containing one, two or three nitrogen heteroatoms, or a 5- or 6-membered heterocyclic ring containing one or two oxygen or sulphur heteroatoms, optionally a nitrogen heteroatom and optionally one or two oxo or thioxo substituents; or X and Y, when ortho to one another, join to form a 5- or 6-membered aliphatic or aromatic ring optionally containing one or two oxygen, sulphur or nitrogen atoms or one, two or three nitrogen atoms; A, B, D, E, G, U and V are independently hydrogen, halogen, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxy, cyano, nitro or trifluoromethyl; R<sup>1</sup> and R<sup>2</sup> are independently hydrogen, C<sub>1-4</sub> alkyl, C<sub>2-8</sub> alkenyl or phenyl; the aliphatic moieties of any of the foregoing being optionally substituted with one or more of halogen, cyano, OR<sup>1</sup>, SR<sup>1</sup>, NR<sup>1</sup>R<sup>2</sup>, SiR<sup>1</sup><sub>3</sub> or OCOR<sup>1</sup> and the phenyl moieties of any of the foregoing being optionally substituted with one or more of halogen, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxy, nitro or cyano; and R<sup>3</sup> and R<sup>4</sup> are independently hydrogen or C<sub>1-4</sub> alkyl.

2. A process for preparing a compound according to claim 1 as herein defined.



3. A fungicidal composition comprising, as an active ingredient, a compound as defined in claim 1 and a fungicidally acceptable carrier or diluent therefor.
4. A process for combating fungi which comprises applying to plants or seeds, or to their locus, a compound as claimed in claim 1 or a composition as claimed in claim 3.

**Patents Act 1977**  
**Examiner's report to the Comptroller under**  
**Section 17 (The Search Report)**

Application number

9200404.3

**Relevant Technical fields**

(i) UK Cl (Edition K ) C2C CKH CKN CKR

(ii) Int Cl (Edition 5 ) C07D

**Databases (see over)**

(i) UK Patent Office

(ii) ONLINE DATABASES : CAS ONLINE

Search Examiner

P N DAVEY

Date of Search

20 FEBRUARY 1992

Documents considered relevant following a search in respect of claims 1-4

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	EP 0398692 A2 (SHIONOGI) see eg page 3 lines 11-41 and page 4, lines 1-6	1-4

Category	Identity of document and relevant passages	Relevant to claim(s)

#### Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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